Longitudinal Gradients in Phosphorus Characteristics in the Minnesota-Upper Mississippi River System

by William F. James, John W. Barko, and Harry L. Eakin

PURPOSE: This technical note describes longitudinal patterns in soluble phosphorus and biologically available particulate phosphorus and equilibrium characteristics for suspended sediment collected at stations located along the Minnesota River (near its headwaters to the mouth) and the Upper Mississippi River (between the Minnesota River confluence and Lock and Dam 2).

BACKGROUND: While soluble phosphorus (P) runoff from watersheds is directly available for algal uptake, particulate forms may also play an important role in the productivity of receiving waters through transformations via recycling pathways that result in conversion of phosphorus to soluble forms. For instance, particulate P (PP), which is loosely bound (i.e., interstitial P, calcium carbonate-bound P, sorbed P; Penn et al. (1995)) and iron-bound (Psenner and Puckso 1988; Nürnberg 1988) can be transformed to soluble P via eH (Mortimer 1971) and pH (Boers 1991) reactions. These particulate P forms may also react with aqueous phases via kinetic processes (adsorption-desorption; Meyer 1979; Mayer and Gloss 1980; Froelich 1988). Labile organic PP runoff can become available to biota as a result of leaching and decomposition.

Labile PP may constitute a significant percentage of the total P in large, complex watersheds exhibiting intensive agricultural land use, such as the Minnesota River (Minnesota-South Dakota) and its various tributaries. In particular, an understanding of how labile PP changes in relative concentration and load as it is transported downstream is needed in the assessment of P budgets of receiving waters. Longitudinal changes in soluble P, PP, and equilibrium characteristics for suspended sediment collected at stations located along the Minnesota River (near its headwaters to the mouth) and the Upper Mississippi River (between the Minnesota River confluence and Lock and Dam 2) were discussed. Potential processes influencing changes in P along the longitudinal axis of the study reach and the relative importance of these loads to downstream receiving waters are discussed.

METHODS: During a period of moderate flow on 5-6 July, 2000, water samples (20-40 L) were collected from the Minnesota River below its confluence with the Chippewa River, Redwood River, Cottonwood River, Blue Earth River, and near its confluence with the Mississippi River (i.e., Ft. Snelling; Figure 1). Water samples were also collected from the Mississippi River approximately 8 miles below its confluence with the Minnesota River (river mile 839.0) and immediately below Pool 2 (river mile 815; Figure 1). Pool 2 of the Mississippi River is located between river miles 847 and 815. Wastewater treatments, which serve the metropolitan area of Minneapolis and St. Paul, discharge into the Minnesota River upstream of the sampling location at Ft. Snelling (i.e., the Chaska, Blue Lake, and Seneca Wastewater Treatment Plants) and upstream of the sampling location on the Mississippi River at river mile 815 (i.e., the Metropolitan Wastewater Treatment Plant or Metro plant). The Metro Plant is the largest of the wastewater treatment plants,
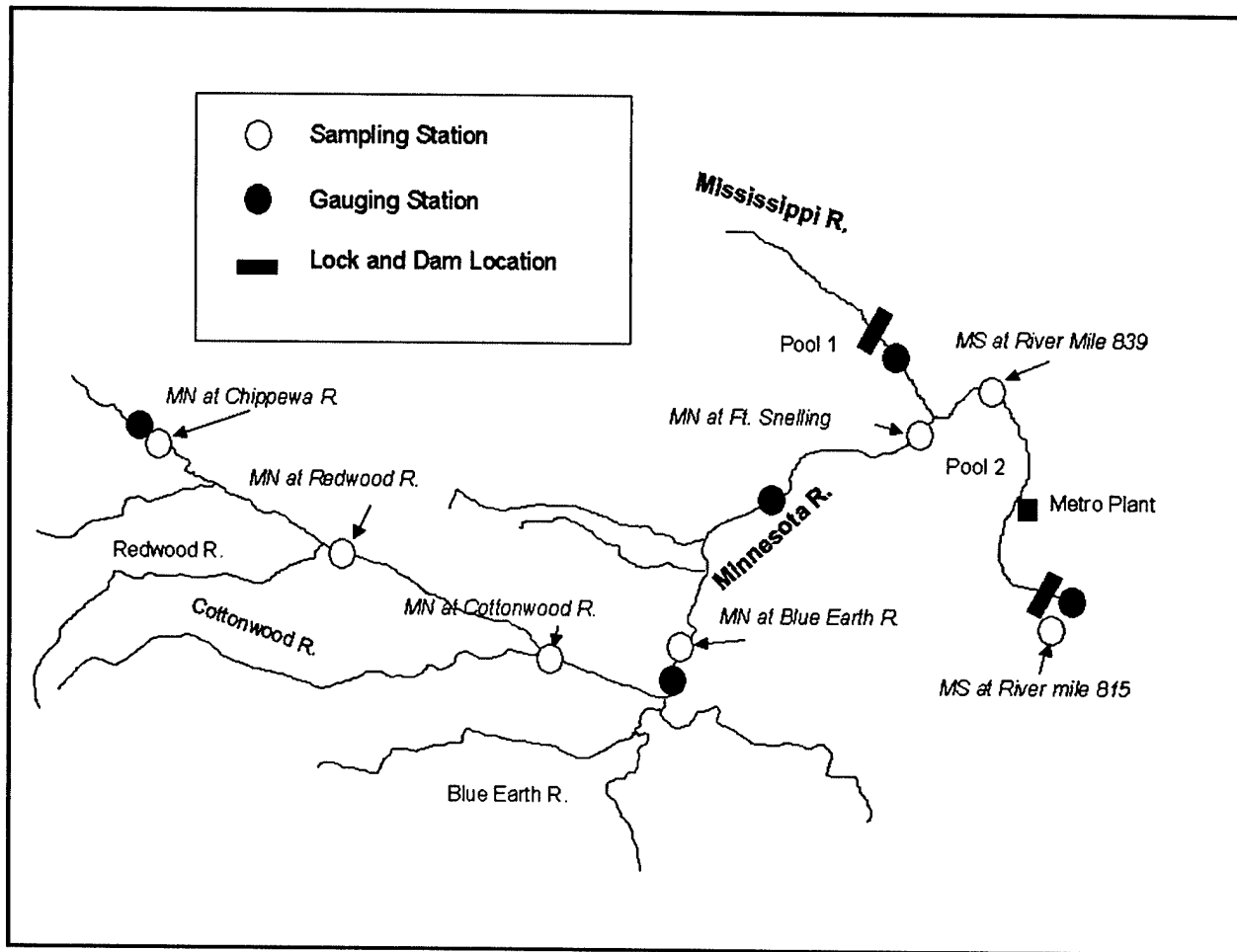
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Figure 1. Area map showing sampling and gauging locations (MS = Mississippi River, MN = Minnesota River)

contributing more than 25 percent of the annual TP contribution to the Mississippi River during average flow years (James et al. 1999). Flow (U.S. Geological Survey and U.S. Army Engineer District, St. Paul) was monitored on the Minnesota River at Montevideo, MN, Mankato, MN, and near the mouth at Jordan, MN, and on the Mississippi River at river miles 839 and 815.

A portion of the sample was filtered through a 0.45-μm filter for soluble constituent determination. Soluble reactive phosphorus (SRP) was analyzed using automated analytical techniques (American Public Health Association) 1992; Lachat Quikchem Autoanalyzer, Zellweger Analytics, Lachat Div. Milwaukee, WI). Total P was analyzed using automated techniques (see above) after digestion with alkaline potassium persulfate (Ameel, Axler, and Owen 1993). Total suspended sediment (TSS) was determined as the mass of particulate material retained on glass fiber filters after drying at 105 $^\circ$C to a constant weight (APHA 1992). Viable chlorophyll was determined fluorometrically (Welschmeyer 1994) following extraction in a dimethyl-sulfoxide:acetone (50:50) mixture at less than 0 $^\circ$C for 12 hr. A modified sequential fractionation of inorganic phosphorus in the sediments was conducted according to Hieltjes and Lijklema (1980), Psenner and Puckso (1988), and Nürnberg (1988) for the determination of inorganic labile PP constituents. Loosely bound and iron-bound P, retained on glass fiber filters, were extracted using ammonium-chloride and bicarbonate-dithionite, respectively. Labile organic PP was determined after extraction with sodium hydroxide followed by digestion

with potassium persulfate (Psenner and Puckso 1988). Labile organic P was calculated as the difference between reactive and nonreactive NaOH-extractable P. Each extraction was filtered through a 0.45-μm filter, adjusted to pH 7, and analyzed for SRP. Total PP was determined using automated techniques following digestion with sulfuric acid, potassium sulfate, and red mercuric oxide (Plumb 1981).

Additional sample was centrifuged at 2500 rpm to concentrate TSS for the determination of P adsorption-desorption characteristics. Sediment aliquots (approximately 500 mg/L dry weight equivalent) were subjected to a series of SRP (KH_2PO_4 as SRP) standards ranging from 0 to 1.0 mg/L (i.e., 0, 0.125, 0.250, 0.500, and 1.00 mg/L) for examination of P adsorption and desorption over a 24-hr period. Untreated well water (groundwater) from the laboratory was used as the water medium because it was phosphate-free. Chloroform (0.1 percent) was added to inhibit biological activity. Replicate (three) sediment systems, containing sediment, groundwater, and known concentrations of SRP, were shaken uniformly for 24 hr, then sampled and analyzed for SRP (APHA 1992). The sediment systems were maintained under oxic conditions at a pH of approximately 8.0 to 8.3 and a temperature of approximately 20 $^\circ$C .

Adsorption and desorption were calculated as the change in SRP (i.e., SRP at 0 hr minus SRP at 24 hr) normalized with respect to sediment dry mass (i.e., mg SRP/g dry mass) and plotted as a function of final SRP concentration (Froelich 1988). The equilibrium phosphate concentration (EPC, mg/L) was calculated as the concentration where net sorption was zero (i.e., often called the crossover point (Mayer and Gloss 1980)). The linear adsorption coefficient (k, L/g) was calculated as the linear slope near the EPC. The native adsorbed phosphate (NAP, mg/g sediment) was calculated as

$$NAP = (k) \cdot (EPC) \tag{1}$$

RESULTS AND DISCUSSION: Sampling occurred during a period of moderately elevated flows in the Minnesota-Mississippi River complex (Figure 2). The actual sampling date fell on the trailing edge of storm-related inflow that had peaked in mid-June. During that period, TSS concentrations were greatest (range = 126 - 190 mg/L) along the Minnesota River between its confluence with the Redwood River and the Blue Earth River (Figure 3). TSS declined at the mouth of the Minnesota River and in Pool 2 of the Mississippi River. Similarly, TSS loading (i.e., the product of flow and concentration) was greatest along the Minnesota River at its confluence with the Blue Earth River and it declined at downstream locations (Table 1). Declines in TSS loading between river miles 839 and 815 were associated with sedimentation of TSS in Pool 2. TSS loading via the Minnesota River at Ft. Snelling accounted for most (80 percent) of the loading measured at river mile 839 of the Mississippi River.

Total P concentrations followed a similar longitudinal pattern as TSS in the Minnesota River (Figure 4). In contrast, SRP concentrations were elevated at the mouth of the Minnesota River and at river mile 815 of the Mississippi River, due most likely to loading from wastewater treatment plants located in the lower Minnesota River basin and in Pool 2 of the Mississippi River (i.e., Metro Plant). As a result of Metro Plant discharges into Pool 2 of the Mississippi River, both total P and SRP loading at river mile 815 (Pool 2 discharge) were high relative to loads measured at river mile 839
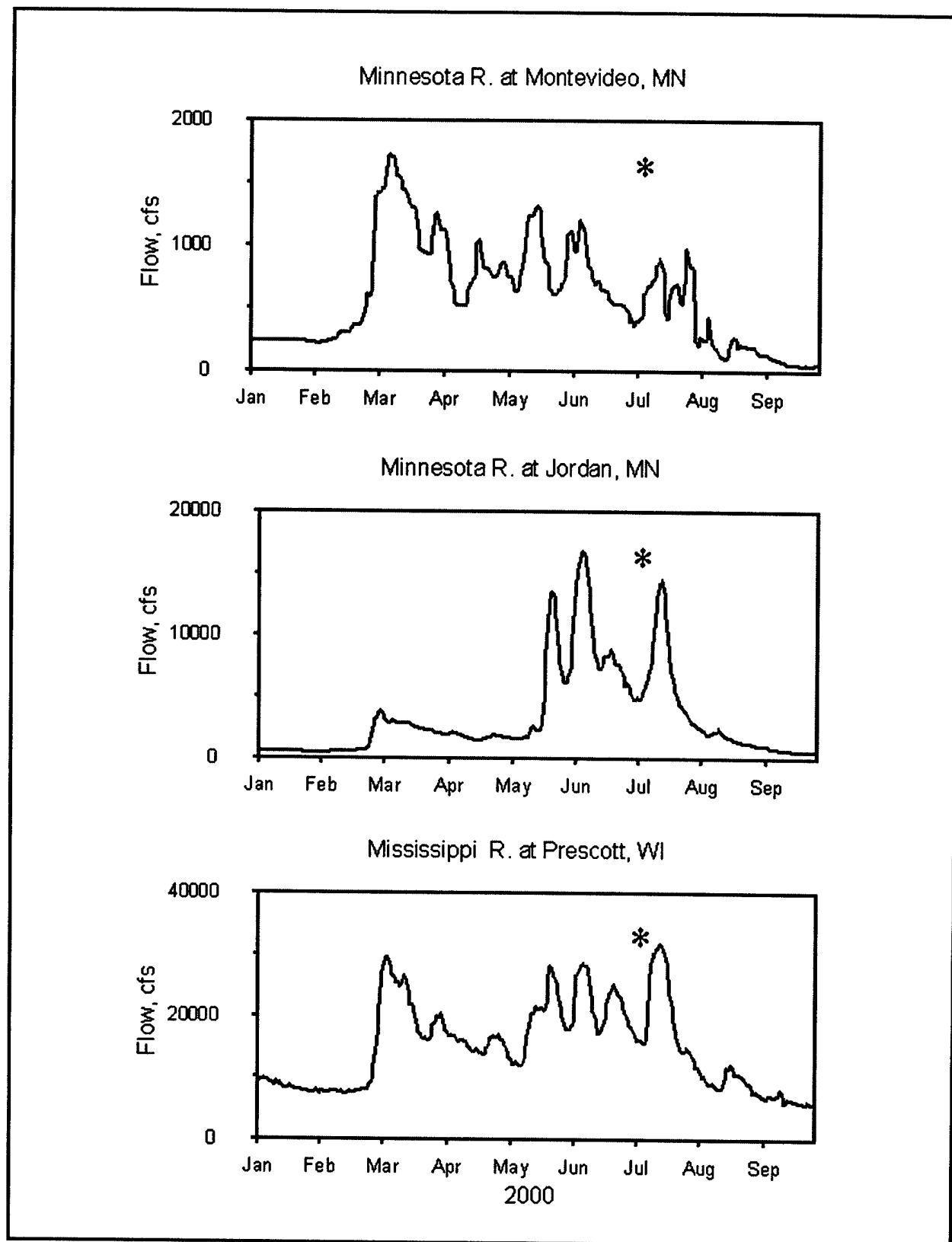
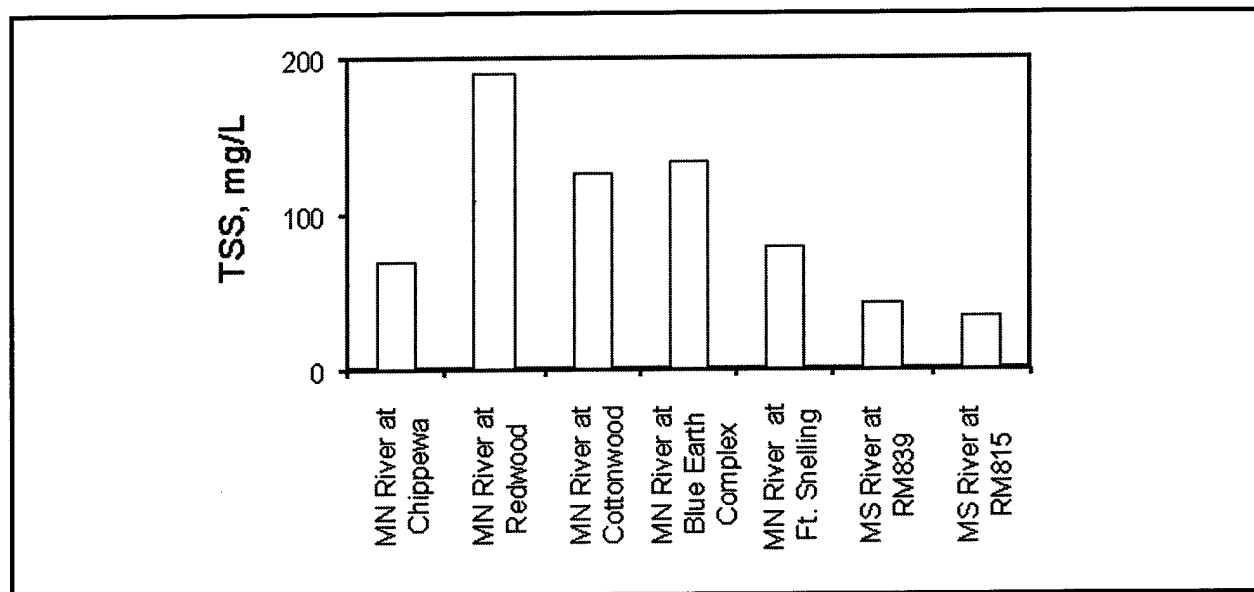Figure 2. Variations in Minnesota and Mississippi River flow in 2000

Figure 3. Variations in total suspended sediment (TSS) concentration along the Minnesota (MN) and Mississippi (MS) Rivers

Table 1
Daily Loading of Total Suspended Sediment (TSS), Total Phosphorus (P), and Soluble Reactive P (SRP) at Various Sampling Stations in Late June, 2000

Location	TSS Load (kg/d)	Total P Load (kg/d)	SRP Load (kg/d)
Minnesota River at Chippewa R. Confluence	69,162	167	28
Minnesota River at Blue Earth R. Confluence	1,766,376	2,920	489
Minnesota River at Ft. Snelling	968,373	2,706	959
Mississippi River at river mile 839	1,218,295	3,869	1,155
Mississippi River at river mile 815	1,010,263	5,473	2,679

(above the Metro Plant), indicating net export of P from Pool 2 on this date (Table 1). SRP concentrations and loads were lower (<0.060 mg/L) at locations on the Minnesota River upstream of Ft. Snelling (Table 1 and Figure 4). Overall, SRP accounted for less than 17 percent of the total P at stations along the Minnesota River located upstream of Ft. Snelling. This percentage increased to more than 30 percent at the Minnesota River at Ft. Snelling and the Mississippi River at river mile 839. SRP accounted for nearly 50 percent of the total P at river mile 815 of the Mississippi River.

Overall, labile PP fractions (i.e., loosely bound PP, iron-bound PP, and organic PP) consistently accounted for approximately 40 percent of the total PP concentration (mg/g of TSS) at all stations, suggesting potential for P recycling (Figure 5). Total and labile PP exhibited peaks along the Minnesota River near its confluence with the Chippewa River and the Cottonwood River (Figure 5). At other locations on the Minnesota River, concentrations of these fractions were lower. In the
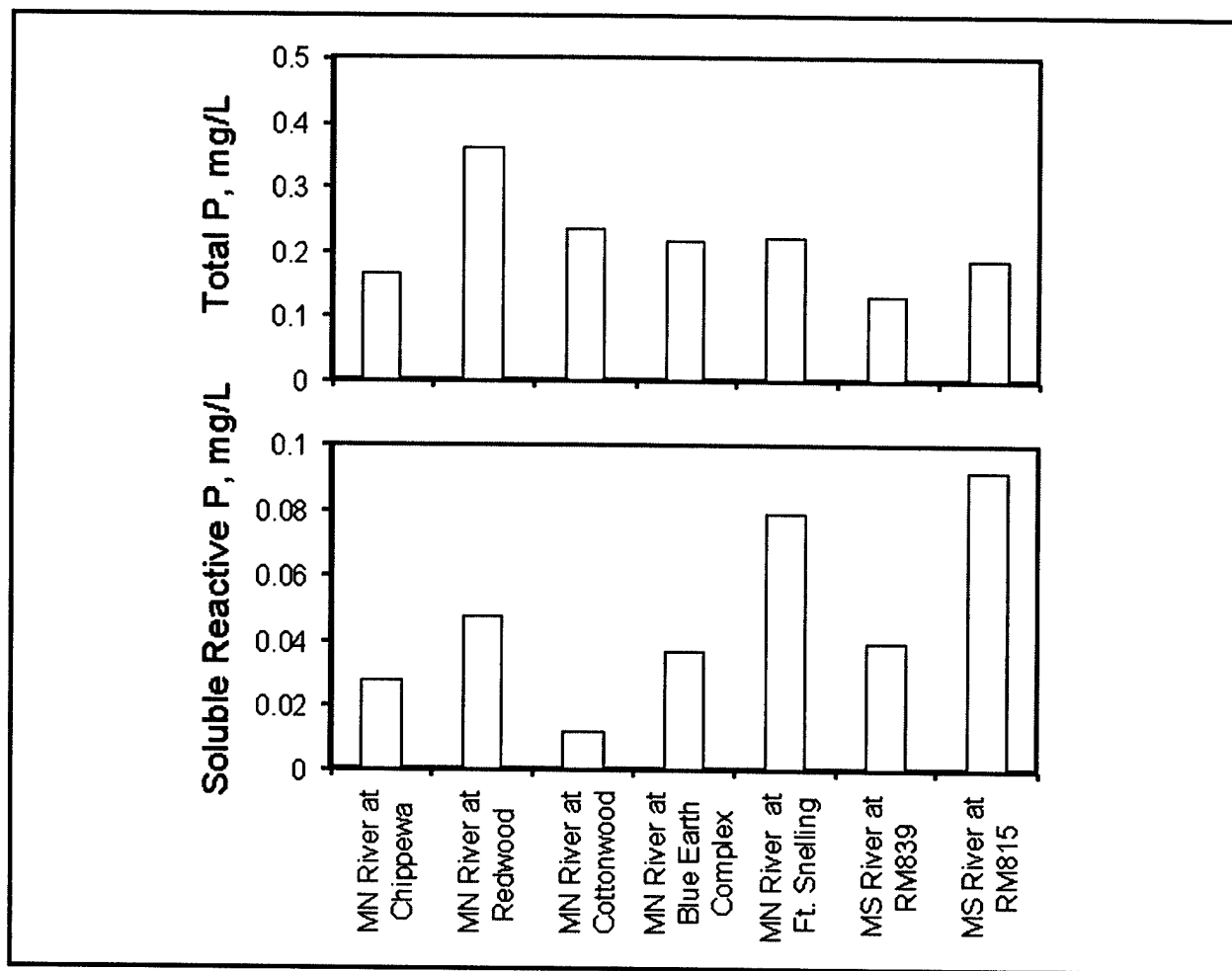
Figure 4. Variations in total phosphorus (P) and soluble reactive P at various stations
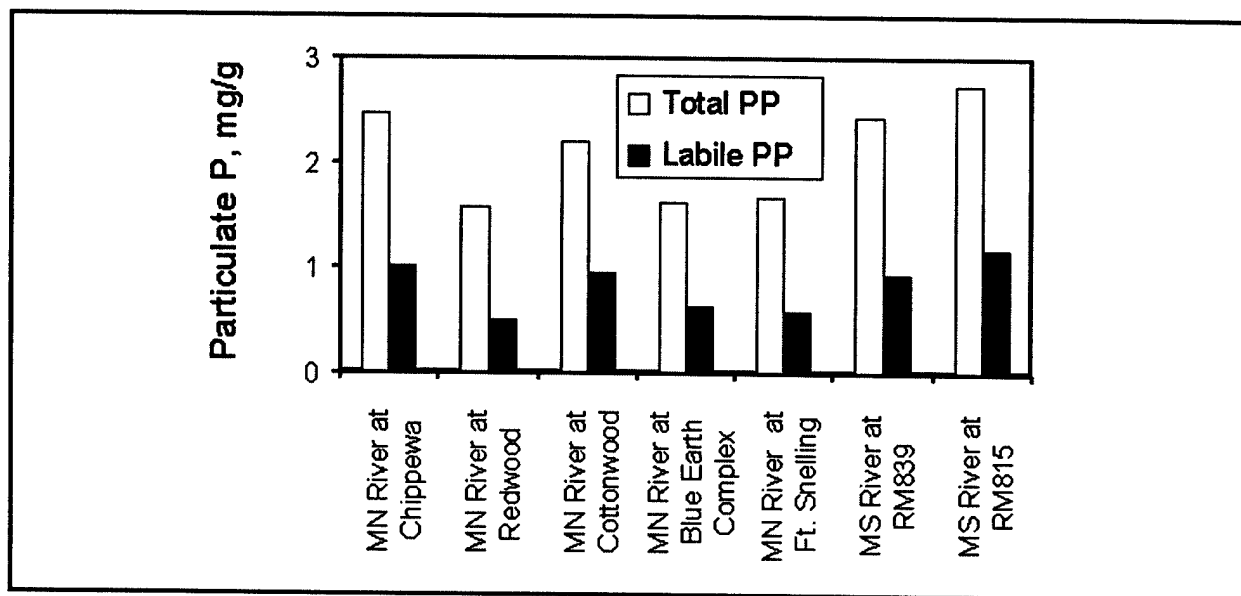
Figure 5. Variations in total particulate phosphorus (PP) and labile PP at various stations. Labile PP represents loosely bound, iron-bound, and organic PP

Mississippi River, concentrations of total and labile PP increased, relative to the concentration observed at the mouth of the Minnesota River (Figure 5). In particular, concentrations of these constituents were elevated at river mile 839 of the Mississippi River, which was located upstream of influences from the Metro Plant. This pattern suggested that loads from the Mississippi River were contributing to PP concentrations at river mile 839. Downstream of the Metro Plant at river mile 815, concentrations of total and labile PP increased further in conjunction with loading from the Metro Plant (Figure 5).

The loosely bound PP fraction accounted for most of the labile PP at nearly all stations (Figure 6). At Minnesota River stations located upstream of Ft. Snelling, labile organic PP was the next greatest fraction, followed by iron-bound PP. In the Minnesota River at Ft. Snelling and in the Mississippi River, the iron-bound PP fraction increased in concentration relative to the labile organic PP fraction (Figure 6). As with total and labile PP, both the loosely bound and iron-bound fraction increased in concentration along the Mississippi River as a result of contributions by the Mississippi River watershed and the Metro Plant.

The EPC was very high along the Minnesota River at its confluence with the Chippewa River and exhibited a trend of decreasing concentration downstream toward Ft. Snelling (Figure 6). The EPC then increased substantially in the Mississippi River at both river miles 839 and 815. The EPC was significantly correlated with NAP, loosely bound PP, and iron-bound PP, but not with labile organic PP (Table 2), suggesting positive relationships between EPC and PP fractions, which are involved in adsorption-desorption processes. However, there was not a significant correlation between EPC and the SRP concentration (Table 2), suggesting that kinetic reactions were not regulating SRP concentrations in the study region at that time. Another factor that could regulate SRP is algal uptake.

Table 2
Correlation Coefficients Between Various Particulate and Soluble Phosphorus (P) Constituents (asterisks indicate significant correlations (Statistical Analysis System 1994))

Variable	(a)	(b)	(c)	(d)	(e)	(f)
(a) Particulate P, mg/g	1					
(b) Loosely bound part. P, mg/g	0.85*	1				
(c) Iron-bound part. P, mg/g	0.81*	0.52	1			
(d) Labile organic part. P, mg/g	0.43	0.13	0.34	1		
(e) Native adsorbed P, mg/g	0.85*	0.72*	0.81*	0.05	1	
(f) Equilibrium P, mg/L	0.90*	0.90*	0.65	0.17	0.92*	1
(g) Soluble reactive P, mg/L	0.08	-0.17	0.58	-0.32	0.39	0.02

The NAP followed the same pattern as EPC (Figure 6). However, it was much lower in concentration than the directly measured loosely bound or iron-bound PP fractions, which interact with aqueous phases via adsorption-desorption reactions (Boström 1984). Differences in concentration may be the result of methodological differences in the determination of NAP versus loosely bound and iron-bound PP. NAP was determined via extrapolation using Equation 1. In contrast, loosely bound and iron-bound PP were measured directly. Nevertheless, there were significant correlations between NAP and these fractions, suggesting that perhaps a portion of the loosely bound and iron-bound PP fractions represented NAP.
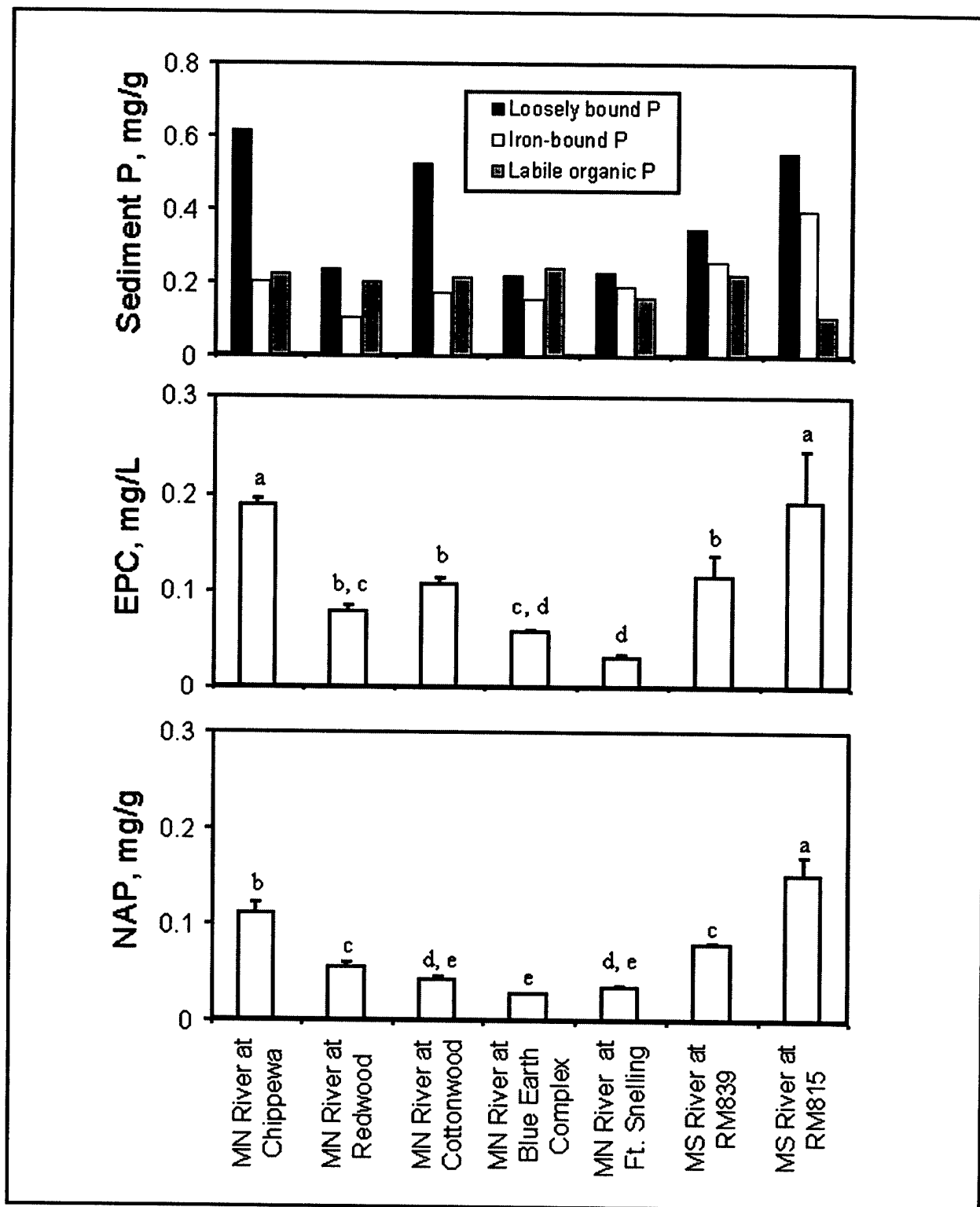
Figure 6. Variations in labile sediment phosphorus (P) concentrations (upper), the equilibrium phosphate concentration (EPC) of suspended sediment (middle), and the native adsorbed P (NAP) of the suspended sediment (lower) at various stations. Different letters in the middle and lower panels indicated significant differences between means based on Duncan's multiple range analysis (SAS 1994). Horizontal bars represent one standard deviation

A significant finding of this study was that much of the PP throughout the study reach was in a labile form that could be recycled as this material moved downstream. Since much of TSS load from the Minnesota River is retained in pools of the Mississippi River (particularly Pool 4 and Lake Pepin), deposition of this labile material could have a very important impact on the P economy and algal productivity of these systems. James, Barko, and Eakin (1999) found that internal P loading from sediments deposited in Lake Pepin was very high (up to 15 mg m^{-2} d^{-1}) relative to many other eutrophic systems (Sas 1989), and could contribute to the P budget and productivity of this system.

Changes in labile PP, which would suggest the occurrence of transformations and recycling, appeared to be most pronounced in the Mississippi River reach of the study area. Here, the EPC and labile PP fractions, which contribute to kinetic processes, increased substantially relative to concentrations in the Minnesota River. Since nearly all of the TSS load in the Mississippi River study area originated from the Minnesota River (Table 1), changes in these variables as TSS entered the Mississippi River may be related to elevated SRP that occurred in Pool 2, and its adsorption to TSS. In particular, the EPC of sediment originating from the Minnesota River at Ft. Snelling (Figure 6) was lower relative to SRP concentrations of the Mississippi River at river mile 815; a condition that would most likely drive adsorption of P onto TSS. Inputs of SRP via the Metro Plant, in excess of the EPC, may in part be driving adsorption of P onto TSS. However, since substantial increases in EPC and labile PP fractions also occurred upstream of the Metro Plant at river mile 839, other sources of P (i.e., Mississippi River and the City of St. Paul) are likely also influencing changes in these variables. This adsorbed P also represents a significant source to the P budget of downstream locations (Lake Pepin) via kinetic processes, which result in desorption of P back into the water column (James, Barko, and Eakin 1999).

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POINTS OF CONTACT: This technical note was written by Messrs. William F. James, John W. Barko, and Harry L. Eakin of the U.S. Army Corps of Engineers, Engineer Research and Development Center, Waterways Experiment Station. For additional information, contact Mr. James (715-778-5896, *jamesw1@svtel.net*) or the Program Managers of the Water Operations Technical Support Program, Dr. Barko (601-634-3654, *John.W.Barko@erdc.usace.army.mil*) or Mr. Robert C. Gunkel (601-634-3722, *Robert.C.Gunkel@erdc.usace.army.mil*). This technical note should be cited as follows:

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